Supplementary information: Thermal conductivity switching in Pd-catalyzed Gd and GdH_2 films upon gasochromic hydrogenation and dehydrogenation

Riko Hirata[1], Yuichiro Yamashita[1,2]*, Takashi Yagi[1,2], Makoto Kashiwagi[1], Satoshi Takeya[2], Yuki Oguchi[3], Fabio Iesari[4], Toshihiro Okajima[1, 4], Naoyuki Taketoshi[1,2] and Yuzo Shigesato[1]*

[1] Graduate School of Science & Engineering, Aoyama Gakuin University, Sagamihara 252-5258, Japan.
[2] National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Central5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.
[3] Center for Instrumental Analysis, College of Science and Engineering, Aoyama Gakuin University, Sagamihara 252-5258, Japan.
[4] Aichi Synchrotron Radiation Center, 250-3, Minamiyamaguchi-cho, Seto, Aichi 489-0965, Japan.

*Corresponding author. E-mail: yuzo@chem.aoyama.ac.jp; yuichiro-yamashita@aist.go.jp

1. XRD patterns in the as-deposited and dehydrogenated

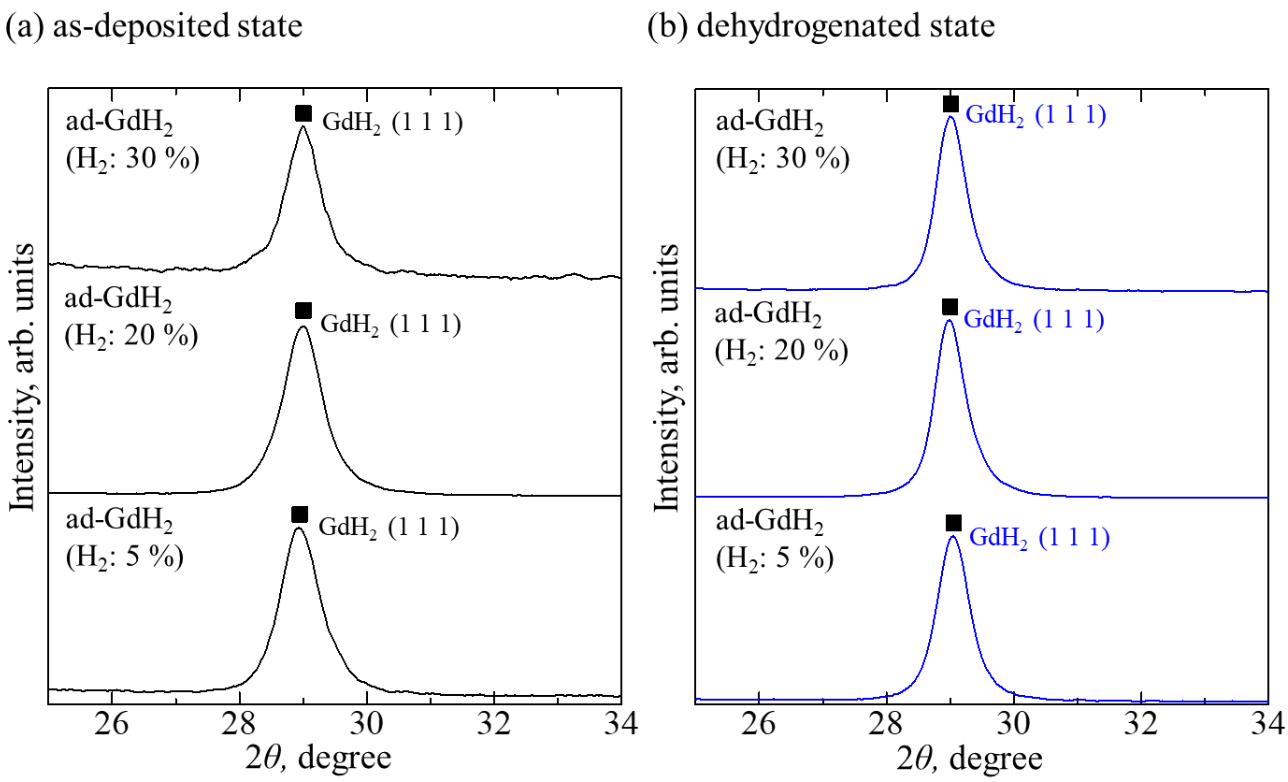

Fig. S1 (a), (b) XRD patterns of the Pd/GdH2 films with the ad-Gd and ad-GdH2 (H_2: 5 %, 20 %, and 30 %) samples for the as-deposited and dehydrogenated states: (a) as-deposited state, (b) dehydrogenated state.

2. XAFS spectra changes upon hydro-/dehydrogenation

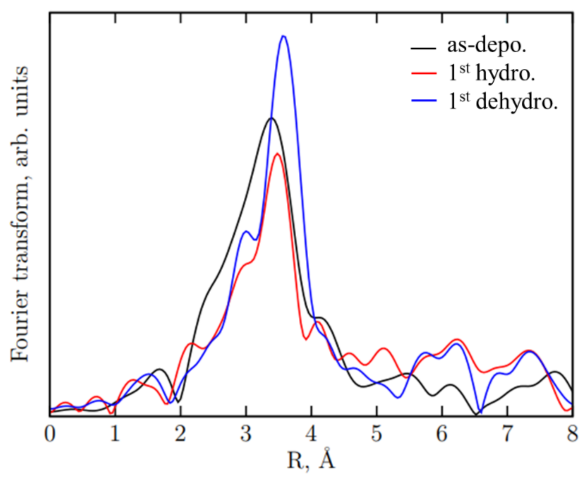

Fig. S2 Fourier transform of the XAFS spectra for the ad-Gd sample in the as-deposited, hydrogenated, and dehydrogenated states.

3. Changes in optical transmittance upon hydro-/dehydrogenation

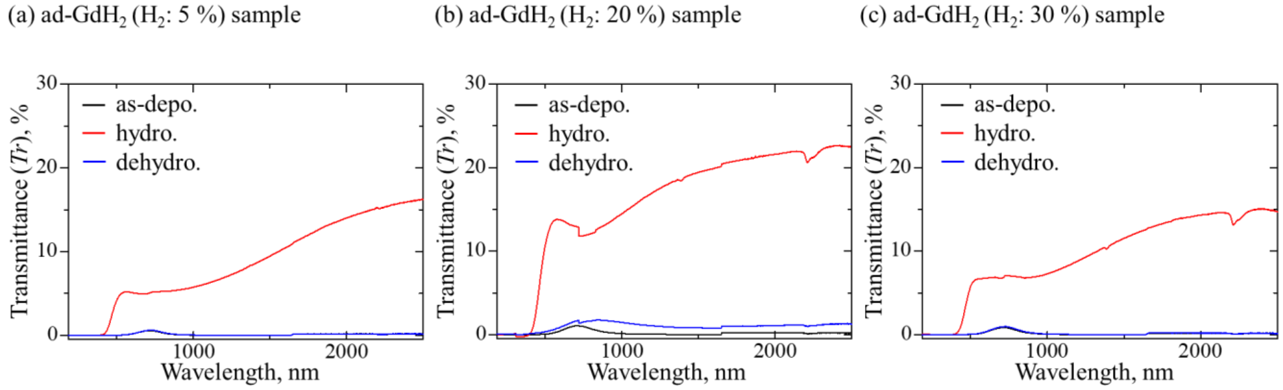

Fig. S3 (a)−(c) Optical transmittance spectra of the Pd/GdH_2 films with the ad-GdH_2 (H_2: 5 %, 20 %, and 30 %) samples, respectively, in the as-deposited, hydrogenated, and dehydrogenated states. In the graphs of (a) and (c), optical transmittance spectra of the as-deposited and dehydrogenated states overlap.

4. In situ time-domain thermoreflectance measurement signal changes upon hydro-/dehydrogenation

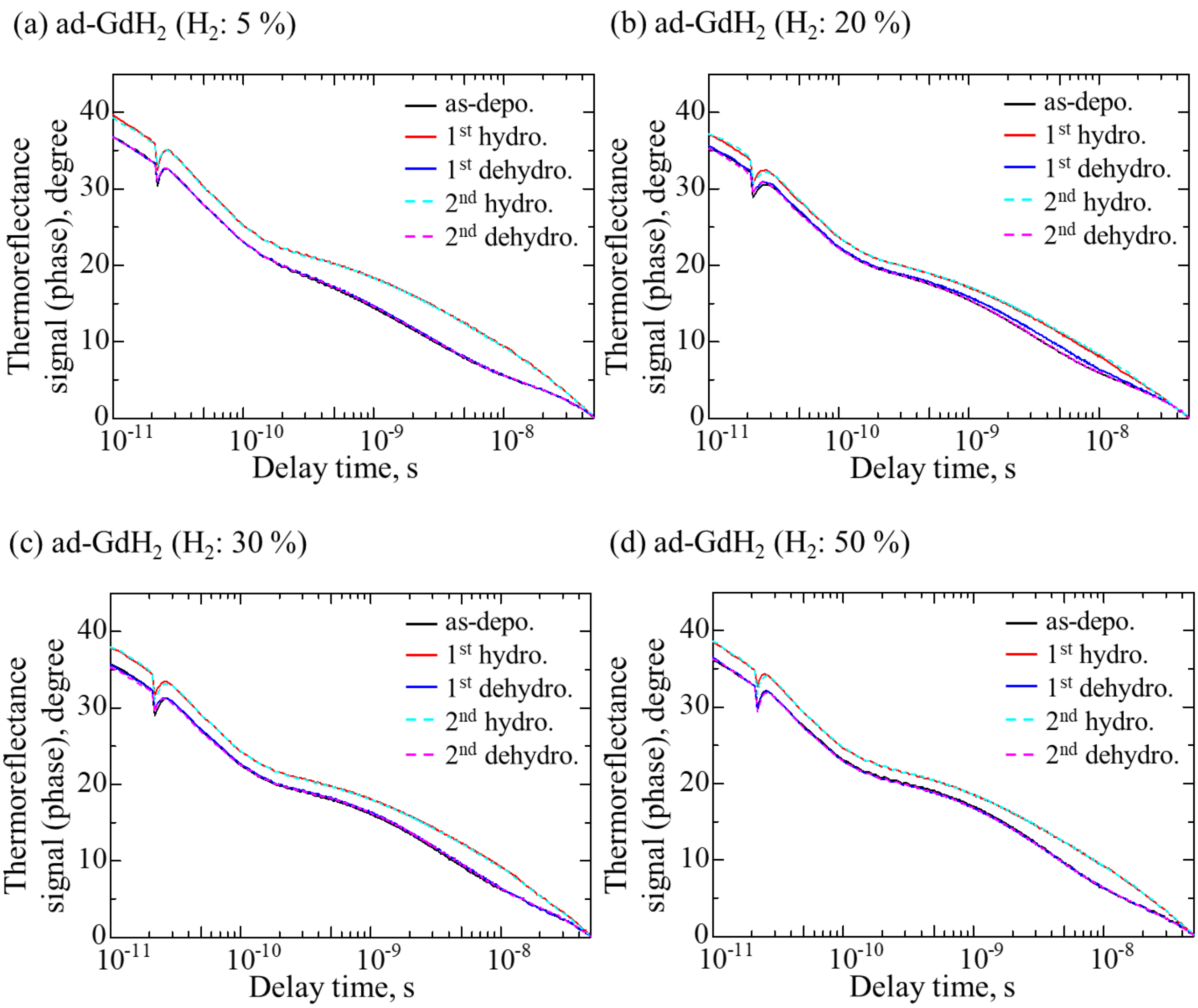

Fig. S4 (a)−(d) Thermoreflectance signals (phase) of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 5 %, 20 %, 30 %, and 50 %) sample, respectively, in the as-deposited, hydrogenated (1st and 2nd), and dehydrogenated (1st and 2nd) states. The thermoreflectance signals of as-deposited and dehydrogenated (1st and 2nd) states in each graph overlap.

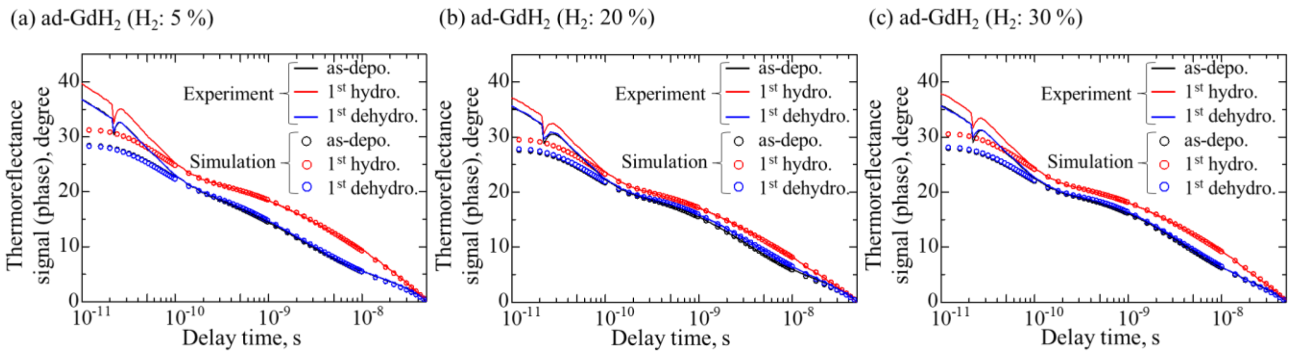

Fig. S5 (a)−(c) Thermoreflectance signals (phase) of Pd/GdH_2/Mo films with the ad-GdH_2 (H_2: 5 %, 20 %, and 30 %) samples, respectively, in the as-deposited, hydrogenated, and dehydrogenated states.

5. Uncertainties of the thermal diffusivity and volumetric heat capacity for Gd and Gd hydrides

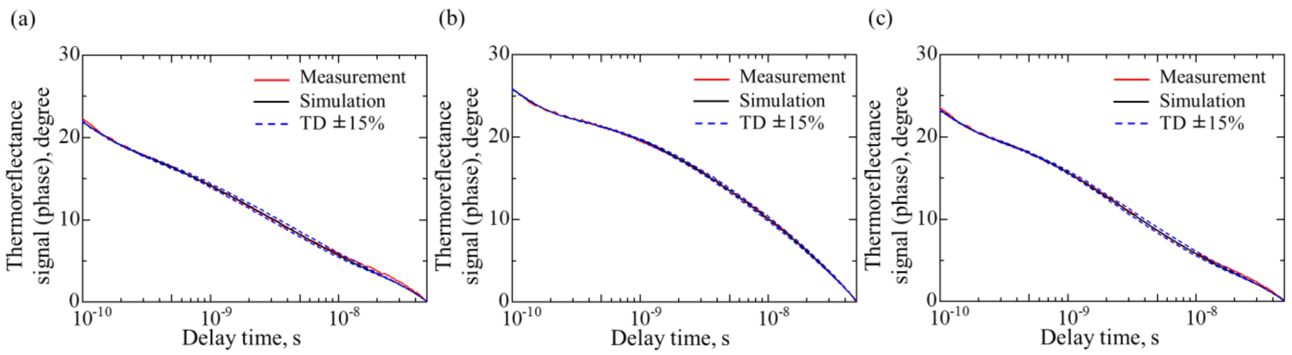

Fig. S6 (a)−(c) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using thermal diffusivities (TD) with ±15 % uncertainties of Pd/Gd/Mo film with the ad-Gd sample: (a) as-deposited state, (b) hydrogenated state, (c) dehydrogenated state.

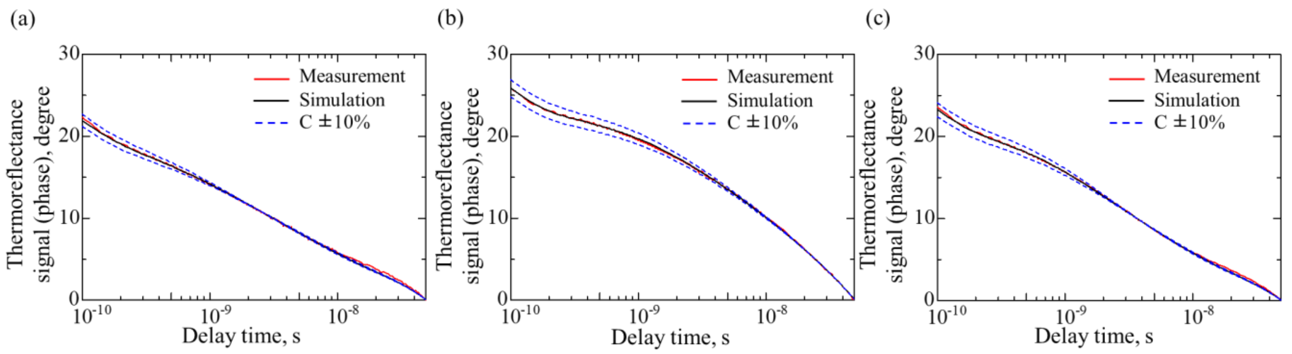

Fig. S7 (a)−(c) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using volumetric heat capacity (C) with ±10 % uncertainties of Pd/Gd/Mo film with the ad-Gd sample: (a) as-deposited state, (b) hydrogenated state, (c) dehydrogenated state.

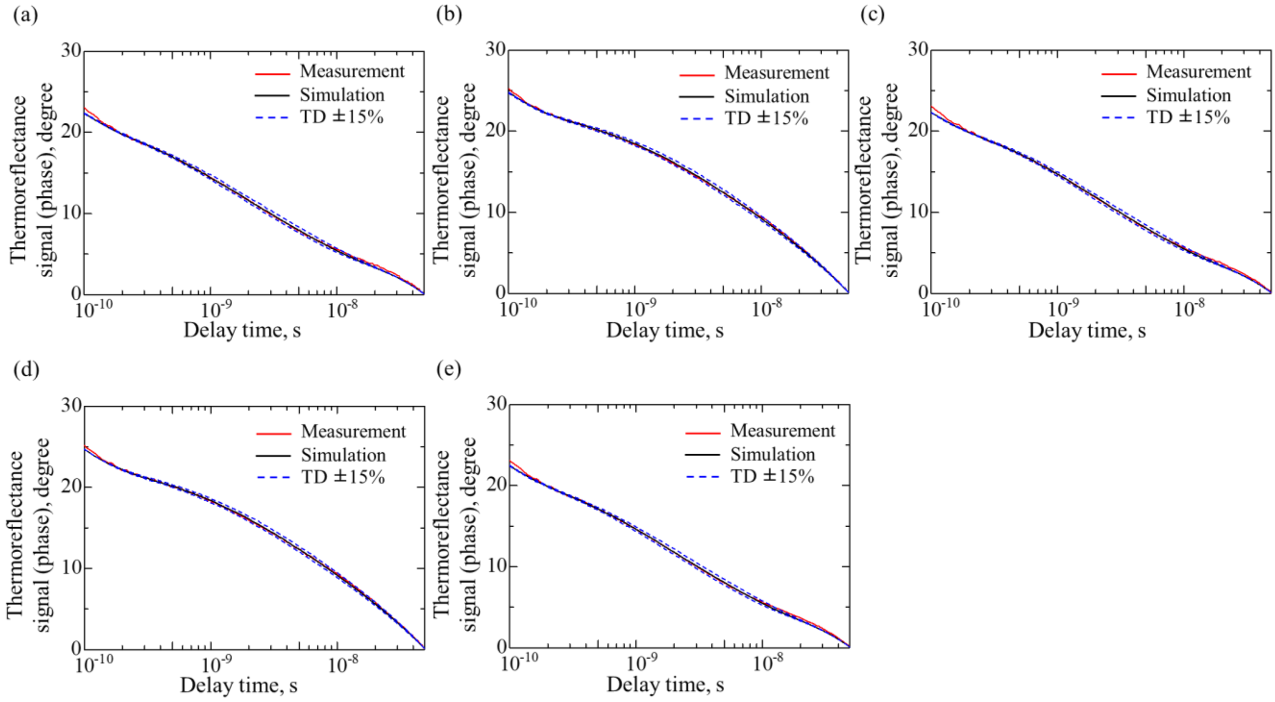

Fig. S8 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using thermal diffusivities (TD) with ±15 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 5 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

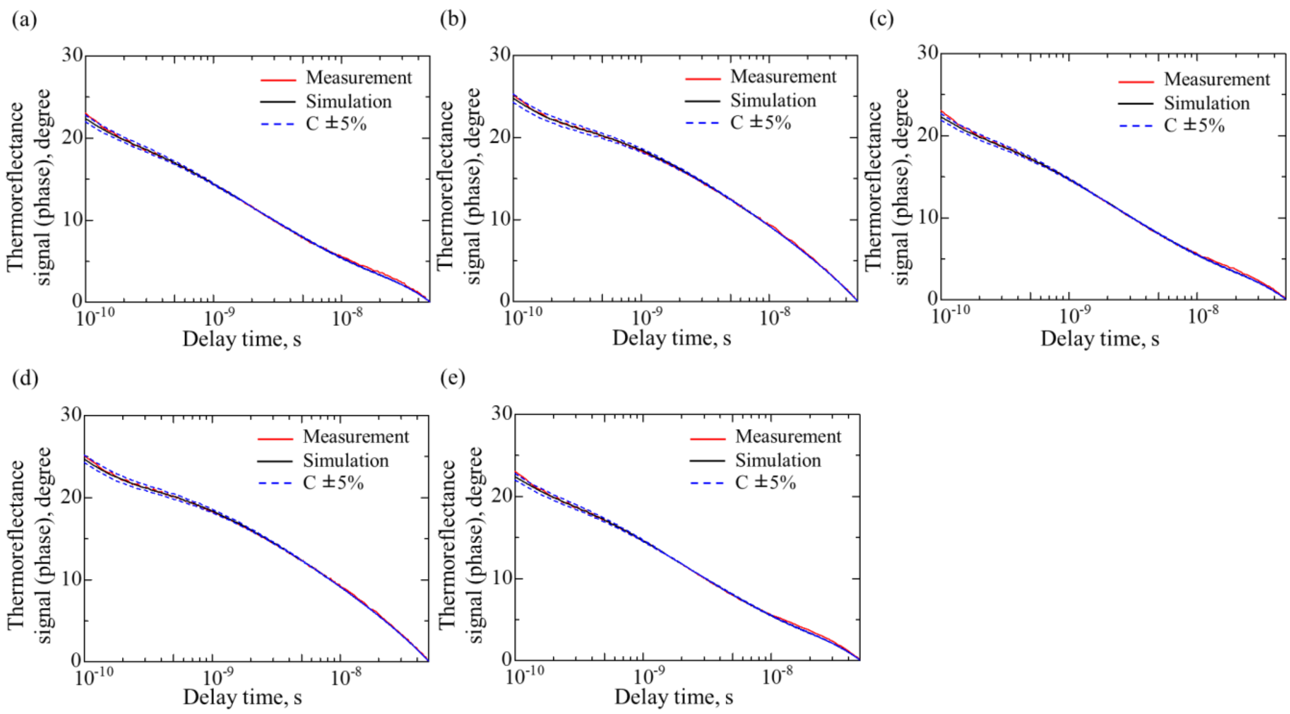

Fig. S9 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using volumetric heat capacity (C) with ±5 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 5 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

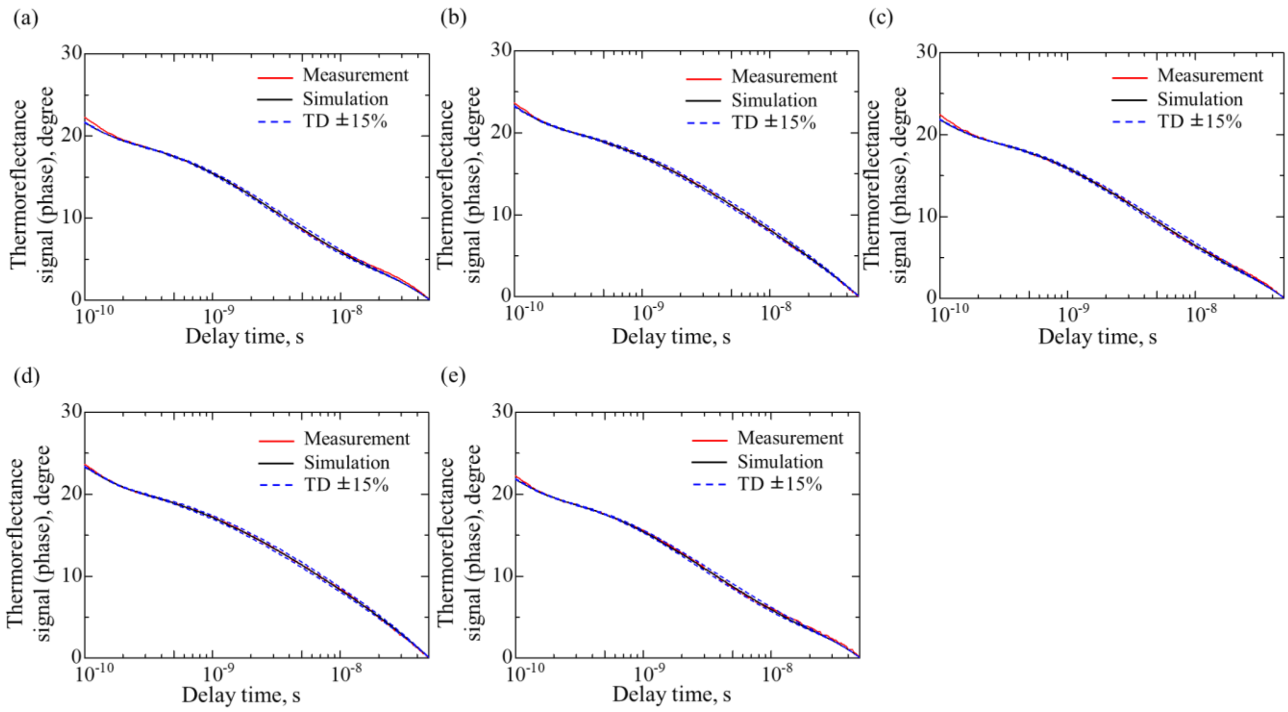

Fig. S10 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using thermal diffusivities (TD) with ±15 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 20 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

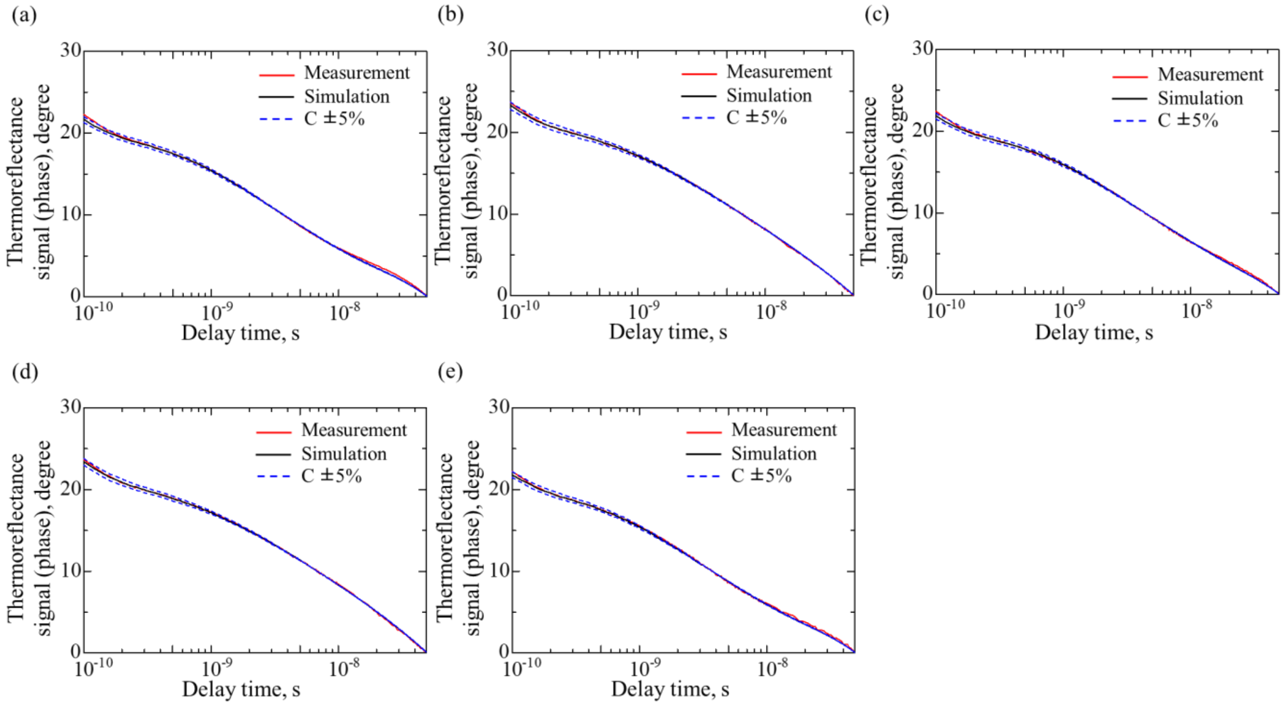

Fig. S11 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using volumetric heat capacity (C) with ±5 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 20 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

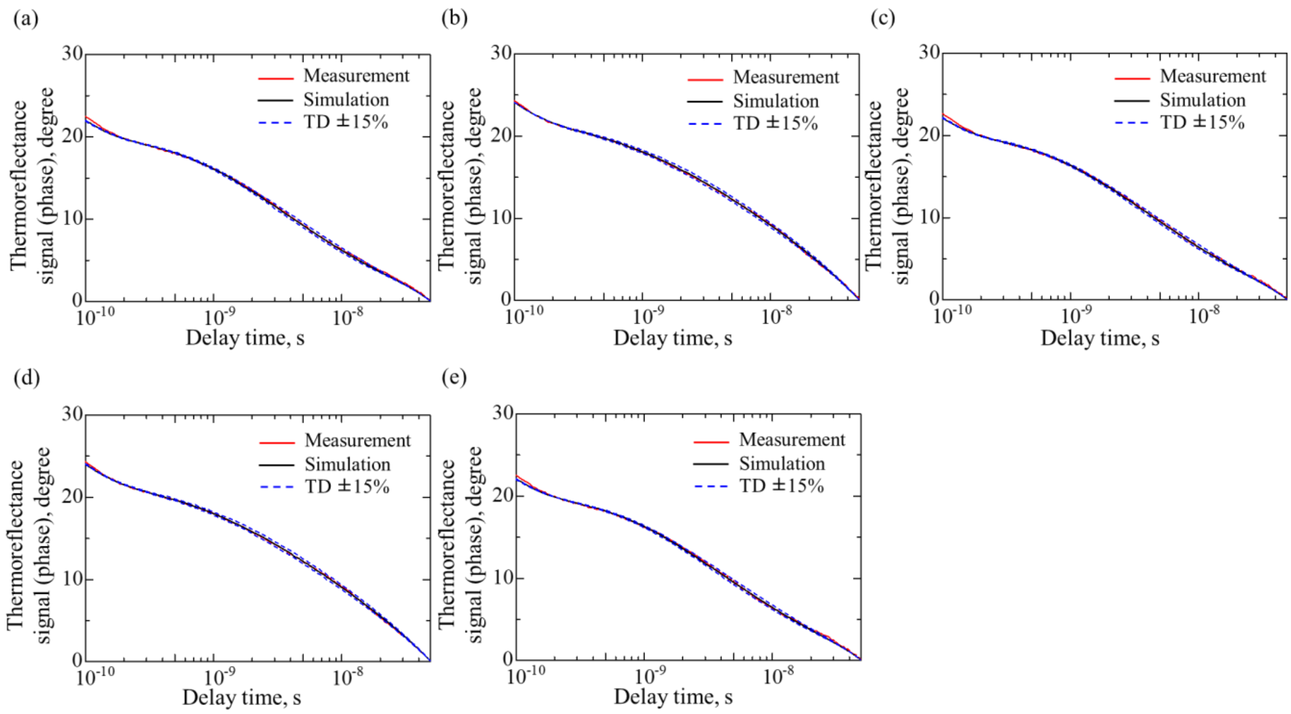

Fig. S12 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using thermal diffusivities (TD) with ±15 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 30 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

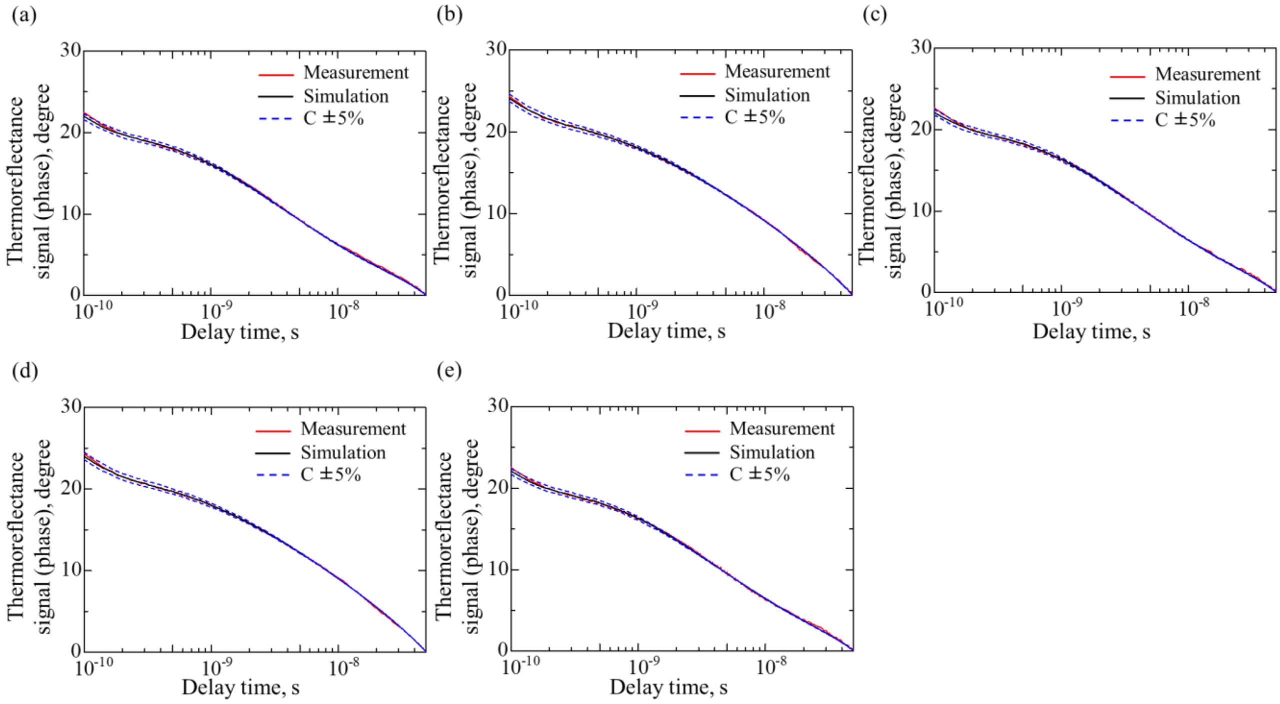

Fig. S13 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using volumetric heat capacity (C) with ±5 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 30 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

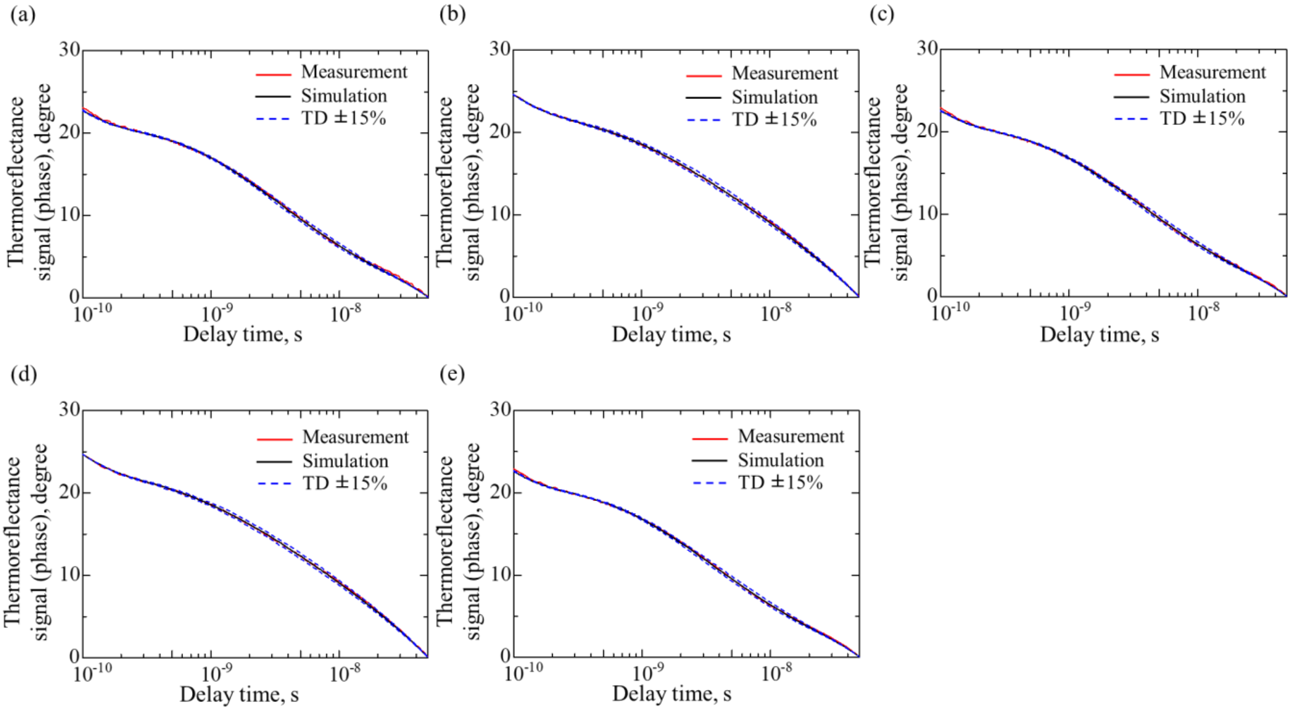

Fig. S14 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using thermal diffusivities (TD) with ±15 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 50 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

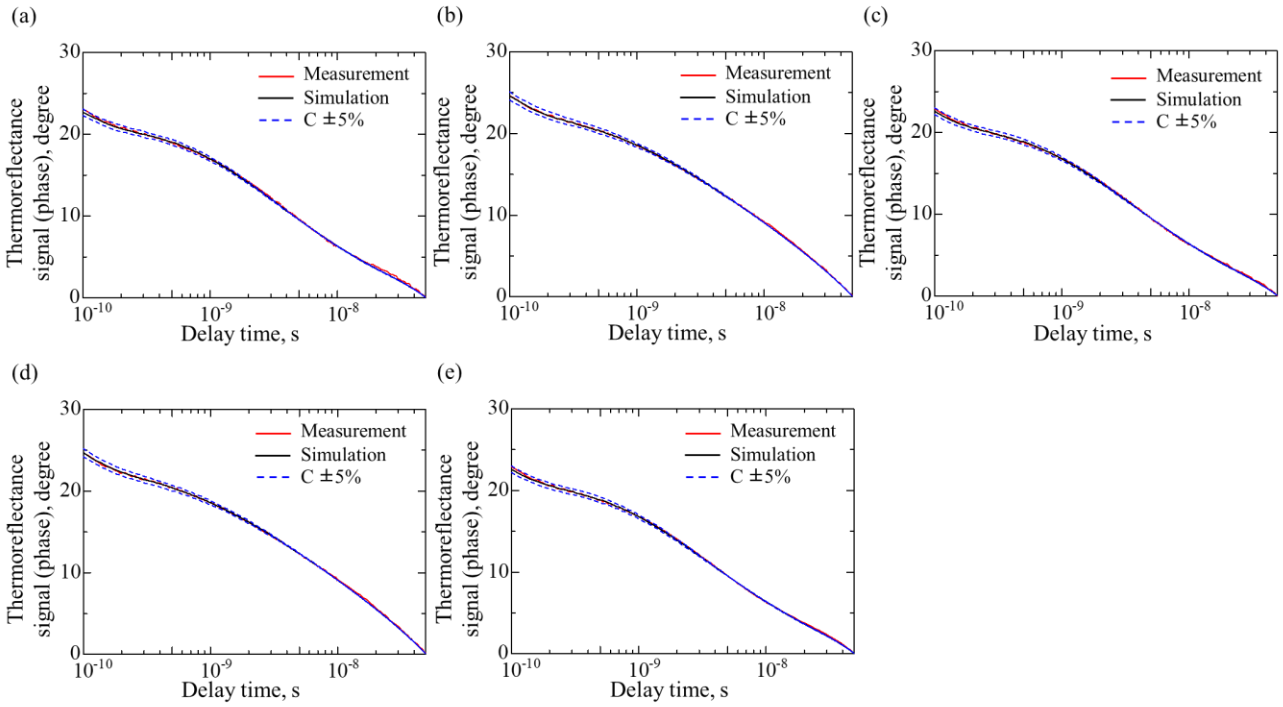

Fig. S15 (a)−(e) Measurement thermoreflectance signals, simulation curves using reported thermal conductivities, and those using volumetric heat capacity (C) with ±5 % uncertainties of Pd/GdH_2/Mo film with the ad-GdH_2 (H_2: 50 %) sample: (a) as-deposited state, (b) 1st hydrogenated state, (c) 1st dehydrogenated state, (d) 2nd hydrogenated state, (e) 2nd dehydrogenated state.

6. Thermal and electrical conductivities upon hydro-/dehydrogenation

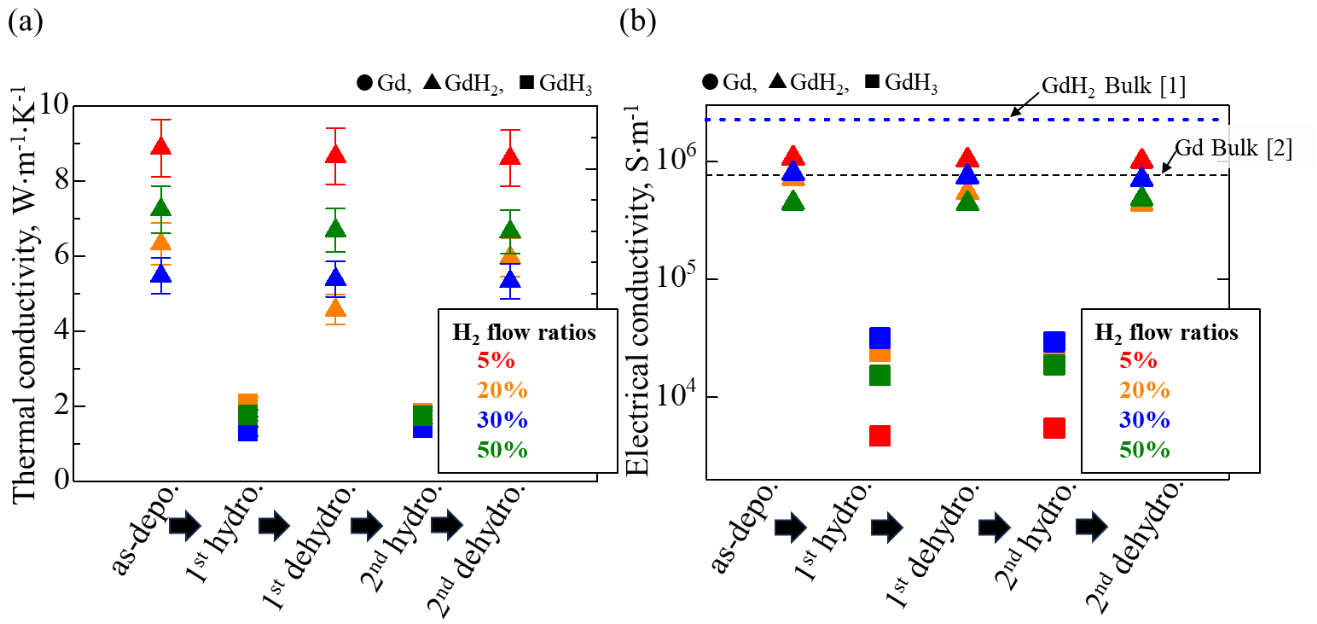

Fig. S16 (a) Thermal conductivities of the ad-GdH_2 (H_2: 5 %, 20 %, 30 %, and 50 %) samples in the as-deposited, hydrogenated, and dehydrogenated states. (b) Electrical conductivities with the ad-GdH_2 (H_2: 5 %, 20 %, 30 %, and 50 %) samples in the as-deposited, hydrogenated, and dehydrogenated states.

7. Comparison of the thermal switching ratio near room temperature for our samples to that of other thermal switching materials

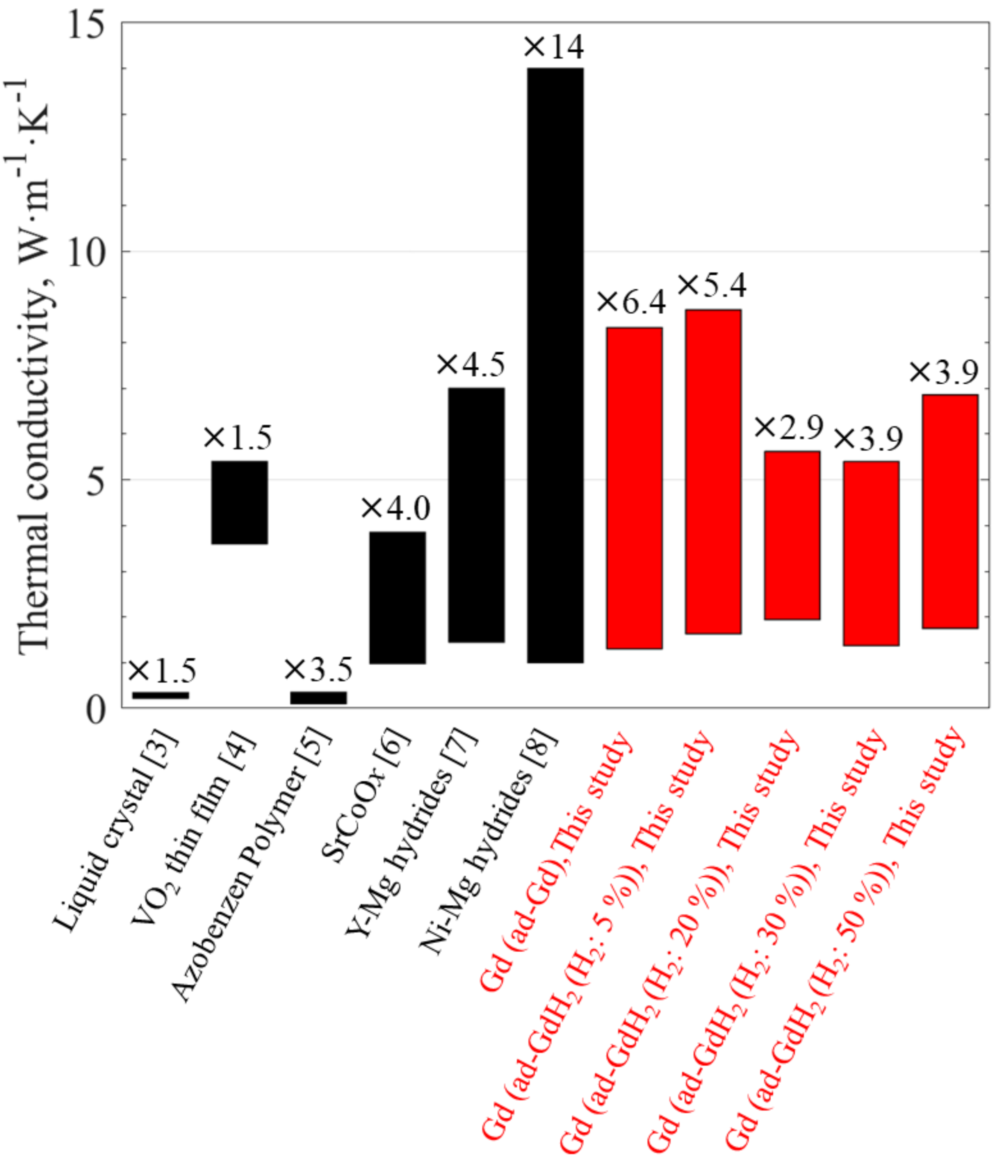

Fig. 17 Summary of the thermal switching ratio near room temperature for various thermal switching materials using the dry process (The labels above each bar denote the thermal switching ratio).

8. Parameters used for fitting to calculate thermal conductivity

Table S1 Common fixed parameters for as-depo., hydro., and dehydro. states

Parameters	Values
Mo/substrate: boundary thermal resistance, m^2 K W^{-1}	2.9×10^{-9}
Mo: volumetric heat capacity, J m^{-3} K^{-1}	2.6×10^{6}
Mo: thermal diffusivity, m^2 s^{-1}	2.1×10^{-5}
Mo: optical absorption coefficient, m^{-1}	4.6×10^{7}
Pd/Gd: boundary thermal resistance, m^2 K W^{-1}	0
Pd: volumetric heat capacity, J m^{-3} K^{-1}	2.9×10^{6}
Pd: thermal diffusivity, m^2 s^{-1}	2.5×10^{-5}
Pd: thickness, m	5×10^{-9}

Table S2 Common fixed parameters (each sample)

	ad-Gd	ad-GdH_2 (H_2: 5 %)	ad-GdH_2 (H_2: 20 %)	ad-GdH_2 (H_2: 30 %)	ad-GdH_2 (H_2: 50 %)
Substrate: thermal effusivity, J m^{-2} $s^{-0.5}$ K^{-1}	1487	1488	1487	1487	1488
Mo: thickness, m	1.02×10^{-7}	9.40×10^{-8}	9.70×10^{-8}	9.70×10^{-8}	9.40×10^{-8}

Table S3 (a)–(e) Fitting parameters and determined properties for each sample

(a) ad-Gd sample

	as-depo.	hydro.	dehydro.
Fixed parameter			
Gd or Gd hydrides: thickness, m	3.00×10^{-7}	3.22×10^{-7}	3.13×10^{-7}
Determined properties			
Gd/Mo: boundary thermal resistance, m^2 K W^{-1}	1.5×10^{-9}	5.5×10^{-9}	3.8×10^{-9}
Gd or Gd hydrides: volumetric heat capacity, J m^{-3} K^{-1}	2.7×10^{6}	3.7×10^{6}	3.0×10^{6}
Gd or Gd hydrides: thermal diffusivity, m^2 s^{-1}	2.7×10^{-6}	3.6×10^{-7}	2.8×10^{-6}

(b) ad-GdH_2 (H_2: 5 %) sample

	as-depo.	1st hydro.	1st dehydro.	2nd hydro.	2nd dehydro.
Fixed parameter					
Gd hydrides: thickness, m	3.07×10^{-7}	3.17×10^{-7}	3.07×10^{-7}	3.17×10^{-7}	3.07×10^{-7}
Determined properties					
Gd hydrides/Mo: boundary thermal resistance, m^2 K W^{-1}	1.6×10^{-9}	4.2×10^{-10}	2.1×10^{-9}	5.4×10^{-10}	1.7×10^{-9}
Gd hydrides: volumetric heat capacity, J m^{-3} K^{-1}	2.8×10^{6}	3.3×10^{6}	2.8×10^{6}	3.3×10^{6}	2.8×10^{6}
Gd hydrides: thermal diffusivity, m^2 s^{-1}	3.2×10^{-6}	4.8×10^{-7}	3.2×10^{-6}	5.0×10^{-7}	3.1×10^{-6}

(c) ad-GdH_2 (H_2: 20 %) sample

	as-depo.	1st hydro.	1st dehydro.	2nd hydro.	2nd dehydro.
Fixed parameter					
Gd hydrides: thickness, m	2.47×10^{-7}	2.55×10^{-7}	2.47×10^{-7}	2.55×10^{-7}	2.47×10^{-7}
Determined properties					
Gd hydrides/Mo: boundary thermal resistance, m^2 K W^{-1}	5.4×10^{-9}	3.0×10^{-9}	5.5×10^{-9}	2.0×10^{-9}	4.6×10^{-9}
Gd hydrides: volumetric heat capacity, J m^{-3} K^{-1}	3.1×10^{6}	3.5×10^{6}	3.2×10^{6}	3.6×10^{6}	3.2×10^{6}
Gd hydrides: thermal diffusivity, m^2 s^{-1}	2.0×10^{-6}	5.8×10^{-7}	1.5×10^{-6}	5.1×10^{-7}	1.9×10^{-6}

(d) ad-GdH_2 (H_2: 30 %) sample

	as-depo.	1st hydro.	1st dehydro.	2nd hydro.	2nd dehydro.
Fixed parameter					
Gd hydrides: thickness, m	2.62×10^{-7}	2.70×10^{-7}	2.62×10^{-7}	2.70×10^{-7}	2.62×10^{-7}
Determined properties					
Gd hydrides/Mo: boundary thermal resistance, m^2 K W^{-1}	6.9×10^{-9}	1.9×10^{-9}	7.2×10^{-9}	2.4×10^{-9}	7.0×10^{-9}
Gd hydrides: volumetric heat capacity, J m^{-3} K^{-1}	3.0×10^{6}	3.6×10^{6}	3.1×10^{6}	3.6×10^{6}	3.1×10^{6}
Gd hydrides: thermal diffusivity, m^2 s^{-1}	2.0×10^{-6}	3.7×10^{-7}	1.8×10^{-6}	4.0×10^{-7}	1.7×10^{-6}

(e) ad-GdH_2 (H_2: 50 %) sample

	as-depo.	1st hydro.	1st dehydro.	2nd hydro.	2nd dehydro.
Fixed parameter					
Gd hydrides: thickness, m	3.01×10^{-7}	3.11×10^{-7}	3.01×10^{-7}	3.11×10^{-7}	3.01×10^{-7}
Determined properties					
Gd hydrides/Mo: boundary thermal resistance, m^2 K W^{-1}	8.0×10^{-9}	2.6×10^{-9}	7.3×10^{-9}	2.3×10^{-9}	7.2×10^{-9}
Gd hydrides: volumetric heat capacity, J m^{-3} K^{-1}	2.9×10^{6}	3.3×10^{6}	2.8×10^{6}	3.3×10^{6}	2.8×10^{6}
Gd hydrides: thermal diffusivity, m^2 s^{-1}	2.5×10^{-6}	5.3×10^{-7}	2.4×10^{-6}	5.2×10^{-7}	2.4×10^{-6}

References

[1] J. P. Burger, J. N. Daou, P. Vajda, J. Less-Common Met. 103, 381–388 (1984)

https://doi.org/10.1016/0022-5088(84)90262-5

[2] R. V. Colvin, S. Legvold, F. H. Spedding, Phys. Rev. 120 (3), 741–745 (1960)

https://doi.org/10.1103/PhysRev.120.741

[3] J. Shin, M. Kang, T. Tsai, C. Leal, P. V. Braun, D. G. Cahill, ACS Marco Lett. 5, 955 (2016)

https://doi.org/10.1021/acsmacrolett.6b00475

[4] H. Kizuka, T. Yagi, J. Jia, Y. Yamashita, S. Nakamura, N. Taketoshi, Y. Shigesato, Jpn. J. Appl. Phys. 54, 053201 (2015) https://doi.org/10.7567/JJAP.54.053201

[5] G. Wehmeyer, T. Yabuki, C. Monachon, J. Wu, C. Dames, Appl. Phys. Rev. 4, 1–32 (2017) https://doi.org/10.1063/1.5001072

[6] Q. Yang, H. J. Cho, Z. Bian, M. Yoshimura, J. Lee, H. Jeen, J. Lin, J. Wei, B. Feng, Y. Ikuhara, H. Ohta, Adv. Func. Mater. 33, 2214939 (2023) https://doi.org/10.1002/adfm.202214939

[7] Y. Yamashita, K. Sugimoto, T. Yagi, M. Kashiwagi, S. Takeya, Y. Oguchi, N. Taketoshi, Y. Shigesato, Appl. Phys. Lett. 123, 232201 (2023) https://doi.org/10.1063/5.0173326

[8] H. Yagi, T. Yagi, Y. Yamashita, M. Kashiwagi, J. Jia, Y. Oguchi, N. Taketoshi, Y. Shigesato, Appl. Phys. Express 16, 095503 (2023) https://doi.org/10.35848/1882-0786/acf6a8